THERMODYNAMIC ANALYSIS OF CONDITIONS GOVERNING THE FORMATION OF ORE MINERALS IN THE PRE-CAMBRIAN PERIOD OF IRON-ORE FORMATION

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A THERMODYNAMIC ANALYSIS OF THE CONDITIONS GOVERNING THE FORMATION OF ORE MINERALS IN THE PRE-CAMBRIAN PERIOD OF IRON-ORE FORMATION

by Yu. P. Mel'nik

A thermodynamic study has been made of certain supposed oxidizing and reduction reactions that occurred in the process of the rock metamorphism of the pre-Cambrian iron ore-formation period. The stability range of the basic ferrous minerals -- siderite, magnetite and hematite -- as determined by the termperature, pressure and concentration (partial pressure) of oxygen, water, carbon dioxide and hydrogen during the mineral-formation period, has been established.

The reduction-oxidation reactions that occurred during the metamorphism of rocks have recently attracted the attention of numerous researchers. The relationship between the natural mineral associations and the assumed partial pressure of free oxygen, as the major oxidizing agent in the rock formation period (Eigster, 1961) have been established in a number of studies on the basis of geological and petrographic observations and thermodynamic calculations. Some researchers also consider water and carbon dioxide as possible oxidizing agents in the natural processes (Korzhinskiy, 1935; Hawley, Robinson, 1948; Mann, 1953).

It follows from these studies that the main oxidizing agent in the meta-morphosed rock was free oxygen whose partial pressure determined the stability range of ferrous minerals. The logarithms of the equilibrium constants (K_p) of the assumed oxidation reactions of siderite and magnetite by free oxygen under any temperatures ascribed to the metamorphic processes are positive, although various authors cite somewhat different K_p values.

In the opinion of the above-mentioned researchers, other possible oxidizers particularly H_2O and CO_2, could hardly have played an important part in the

metamorphism, inasmuch as the equilibrium constants calculated by J. Hawley and S. Robinson (1948) for the assumed reaction $2Fe_3O_4 + CO_2 \rightleftarrows 3Fe_2O_3 + CO$ revealed the practical impossibility of oxidizing magnetite by carbon dioxide within a temperature range of 25-500° (the calculated magnitude of K_p is within the range of $10^{-18.9} - 10^{-7.7}$). According to B. Mann (1953), in the case of the assumed oxidation reaction of magnetite, $2FE_3O_4 + H_2O \rightleftarrows 3Fe_2O_3 + H_2$, a K_p value even above 600° does not exceed 1.9×10^{-4}, and the K_p value is still smaller at lower temperatures. Comparing the oxidation reaction of Fe_3O_4 by water and CO_2, B. Mann came to the conclusion that the oxidation of magnitude by carbon dioxide under natural conditions was improbable, but water could have served as an oxidizer in some cases.

It should be pointed out that the majority of the published studies deal only with the assumed oxidation reactions of magnetite but do not discuss the possible oxidation of other minerals containing ferrous iron in a medium devoid of free oxygen. Such calculations, based primarily on the assumed oxidation reactions of magnetite, prompted the belief among the geologists in the predominant role of free oxygen in the formation of particular minerals containing elements of variable valence. Without denying the role of free oxygen in the formation of the basic ore minerals of the iron ore formations, we would like to call attention to the role of water as a possible oxidizing agent in the metamorphism, and take a closer look at the reduction-oxidation reactions which explain the origin of the major paragenetic mineral associations of ferruginous quartzites and ores in the presence of water.

The Investigation Methods

We have made a theoretical study of the assumed oxidation reactions of siderite and magnetite, as the basic minerals containing ferrous iron, by free oxygen and water in a temperature range of 25-500°.

In our calculations we used Gibb's basic equation:

$$\Delta Z = \Delta H - T \Delta S \qquad (1)$$

the conventional symbols of the thermodynamic values were those proposed by

V. A. Koreyev (1959). Using this equation under standard conditions (T_o 298°K),

we determined the magnitude ΔZ_o of the reaction, and then calculated the

equilibrium constant by the equation of the chemical reaction isotherm:

$$\ln K_{p_o} = -\frac{\Delta Z_o}{RT} \qquad (2)$$

At higher temperatures, the magnitude $\Delta H = f(t)$ was first determined on

the basis of the general equation:

$$\Delta H = \int \Delta C_p dT \qquad (3)$$

by substituting in it the standard equation of heat capacity for a given reaction:

$$\Delta C_p = \Delta a + \Delta b \cdot T - \Delta c' \cdot T^{-2} \qquad (4)$$

and the following integration:

$$\Delta H = \Delta a \cdot T + \frac{\Delta b}{2} \cdot T^2 + \Delta c' \cdot T^{-1} + C_h. \qquad (5)$$

with the temperature unknown, the equilibrium constant of the reaction was found

by the equation of the reaction isobar:

$$\ln K_p = \int \frac{\Delta H}{RT^2} dT \qquad (6)$$

after the substitution in it of equation $\Delta H = f(T)$ in the form of (5); after

the transformations, the change to decimal logarithms and the substitution of a

numerical value of the gas constant R, it looked like the following:

$$\lg K_p = \frac{\Delta a \cdot \lg T}{1,987} + \frac{\Delta b \cdot T}{9,1516} - \frac{\Delta c'}{9,1516 \cdot T^2} - \frac{C_h}{4,5758 \cdot T} + C. \qquad (7)$$

The first step in the solution of that basic equation was to compute the

integration constant, C_h of equation (5) by the calculated magnitude of the en-

thalpy increment, the ΔH_o reaction at 298°K. The integration constant of

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finite equation (7), C magnitude, was determined by the calculated magnitude of lg K_{p_0} for standard conditions on the basis of equation (2).

For some reactions it is impossible to make such precise caculations inasmuch as the factors of the thermal capacity equation (4) are not known for all the substances. In these cases we confined ourselves to the calculations with the generally accepted assumption that the thermal capacities of the reacting substances do not change with the temperature. The calculations were based on the following equation:

$$ \lg K_p = \frac{\Delta C_p \cdot T_o - \Delta H_o}{4,5758 \cdot T} + \frac{\Delta C_p \cdot \lg T}{1,987} + C \tag{8} $$

The difference in the values lg K_p obtained by the simplified calculation according to equation (8) and the more precise calculation according to equation (7) within the known temperature range of all the examined reactions is very insignificant.

These calculations are somewhat labor-consuming, but they facilitate, after a series of preparatory operations, a very precise calculation of the equilibrium constant of the reaction at any preset temperature. There are also other methods of calculating ΔZ and K_p reactions (Vladimirov, 1956; Nikolayev and Dolivo-Dobrovol'skiy, 1961) in which previously tabulated values are used to simplify calculations. But when these methods are used, it is impossible to calculate the K_p values at intermediate temperatures for which there are no calculated coefficients; for example, there are none for 200° or 250°, but there are for 220°.

Inasmuch as most of the studied reactions involved various molecular quantities of gaseous substances on the right and left sides of the reaction equations, the change in pressure should produce a substantial effect on the direction of the reactions and the composition of the equilibrium gas mixture.

A number of petrological studies (Korzhinskiy, 1935; Nikolayev and Dolivo-Dobrovol'skiy, 1961) deal with the metamorphic reactions involving the

absorption or emission of a gas phase, as for example the known reaction of wollastonite formation: $CaCO_3 + SiO_2 \rightleftarrows CaSiO_3 + CO_2$. For such reactions involving a gas phase the equilibrium is determined by the partial pressure of a pure gaseous component, and in the above-cited example, in the case of equilibrium, the CO_2 pressure should be a constant value for each given type of temperature. But there is insufficient reference in geological literature to similar cases when the general pressure is determined not by a partial pressure of one gas component but by the pressure of a gas mixture participating in the reaction. In the reactions involving the participation of three and more gas components, the calculation of the equilibrium gas composition by the use of graphic methods (Ellis, 1957; Wyllie, Tuttle, 1960) is very complicated. Thus to account for the effect of the pressure in such reactions and to determine the equilibrium composition of the gas mixture under wide range of temperatures and pressures, it would be more practical to draw up special equation expressing the relationship between the equilibrium constants and the composition of the gas mixture. The methods of such calculations are outlined in greater detail in special studies, such as the one by A. A. Vvedenskiy (1960). The calculation process can be illustrated in relation to the following reaction we have studied, $3FeCO_3 + H_2O_r \rightleftarrows Fe_3O_4 + 3CO_2 + H_2$, in which the equilibrium mixture was measured in gram-molecules:

$$
\begin{aligned}
H_2 &= x \\
H_2O &= 1 - x \\
CO_2 &= 3x \\
\hline
\Sigma &= 1 + 3x
\end{aligned}
$$

According to Dalton's law, the partial pressures of the components of the equilibrium mixture should amount to:

$$P_{H_2} = \frac{x}{3x+1} \cdot P; \quad P_{CO_2} = \frac{3x}{3x+1} \cdot P; \quad P_{H_2O} = \frac{1-x}{3x+1} \cdot P,$$

where P is the total pressure in the system.

The equilibrium constant of the reaction under consideration, expressed in partial pressure of gas components, amounts to:

$$K_p = \frac{\left(\frac{3x}{3x+1} \cdot P\right)^3 \left(\frac{x}{3x+1} \cdot P\right)}{\left(\frac{1-x}{3x+1} \cdot P\right)} \cong \frac{27x^4 \cdot P^3}{(3x+1)^3 (1-x)} \,, \tag{9}$$

The simplest way of solving the resulting equation is by the inspection method, that is by substituting the possible values x in the interval from 0 to 1, (the values $x < 0$ and $x > 1$ in the accepted value of x are devoid of any physical meaning) and any unknown magnitudes of the total pressure P, for example, 1, 5, 50, 100, 500, 1,000, 5,000 and 10,000 atmospheres. The logarithm was taken of the equation beforehand for the convenience of calculation, and it looked like the following:

$$\lg K_p = 1,4314 + 4\lg x - 3\lg(3x+1) - \lg(1-x) + 3\lg P. \tag{10}$$

The resulting calculations are then used to draw up a nomograph for the graphic solution of the equation (Fig. 1) for each reaction. To this end, the curves obtained from the solution of equation (10) and showing the relationship between the composition of the equilibrium mixture from the various pressures and the $\lg K_p$ are combined on the diagram with the curve indicating the dependence of $\lg K_p$ on the temperature which was obtained in the solution of equation (7) or (8).
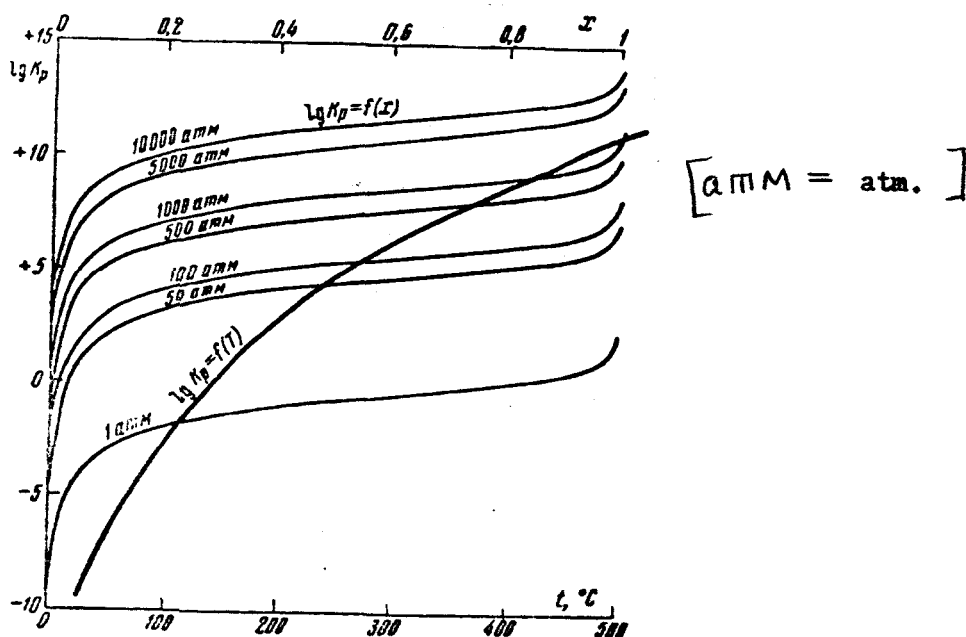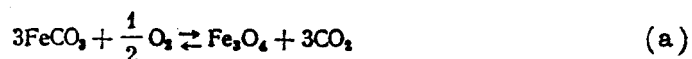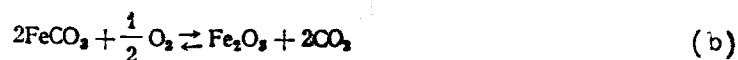

Fig. 1. A nomogram for the graphic solution of equation (10) for the oxidation reaction of siderite to magnetite by water vapor

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Under consideration in this study are the possible reactions of solid phases (siderite and magnetite) with gaseous oxidizers by free oxygen and water vapor as well as by liquid water. All the calculations are based on the assumption that the gaseous components possess the properties of ideal gas. Such an assumption is made in the majority of the petrological and physico-chemical studies (Korzhinskiy, 1935; Nikolayev, 1952: Krauskopf, 1961: Garrels, 1962). Under high pressures, when the deflection of the gas properties from the ideal gas are significant, the calculated equilibrium constants should differ from the experimental ones. However, in the reactions under consideration, the preliminary calculations made by the M. G. Sonikberg method (1960) show that in the high pressure region the difference between K_p and K_f (equilibrium constant expressed by gas volatility) is not large enough to change the course of the reactions. In the area of supercritical pressures and temperatures below 400°, the calculated equilibrium constants for the reactions involving liquid water are probably closer to the two constants than the equilibrium constants of the reactions involving gaseous water even if they include the appropriate corrections for the deviations of the water vapor from the characteristics of ideal gas. Characteristically, the equilibrium constant with the corrections calculated for the reactions involving water vapor has an intermediate value between the K_p, obtained for a reaction with liquid water, and K_p for a reaction with ideal water vapor.

The Calculation Results

In all the oxidation reactions of siderite and magnetite by free oxygen, the logarithms of the equilibrium constants were positive in the studied temperature range of 25-500°. Presented in Fig. 2 are the curves lg K_p f(T) of the following assumed reduction-oxidation reactions:

$$3FeCO_3 + \frac{1}{2} O_2 \rightleftarrows Fe_3O_4 + 3CO_2 \qquad (a)$$

$$2FeCO_3 + \frac{1}{2}O_2 \rightleftarrows Fe_2O_3 + 2CO_2 \qquad (b)$$

$$2Fe_3O_4 + \frac{1}{2}O_2 \rightleftarrows 3Fe_2O_3 \qquad (c)$$

The equilibrium constants are somewhat reduced with rising temperature, but even at $500°$ they are still very high.

Expressing the equilibrium constants of the reactions under consideration, as for example reaction (a), by partial gas pressures:

$$K_p = \frac{(P_{CO_2})^2}{(P_{O_2})^{\frac{1}{2}}}$$

it is possible to calculate the equilibrium partial pressure of oxygen with the temperature and general pressure magnitudes remaining unknown (assuming that $P_{Gen.} = P_{CO_2}$). At $500°$ and 1 atmosphere, this calculated partial oxygen pressure
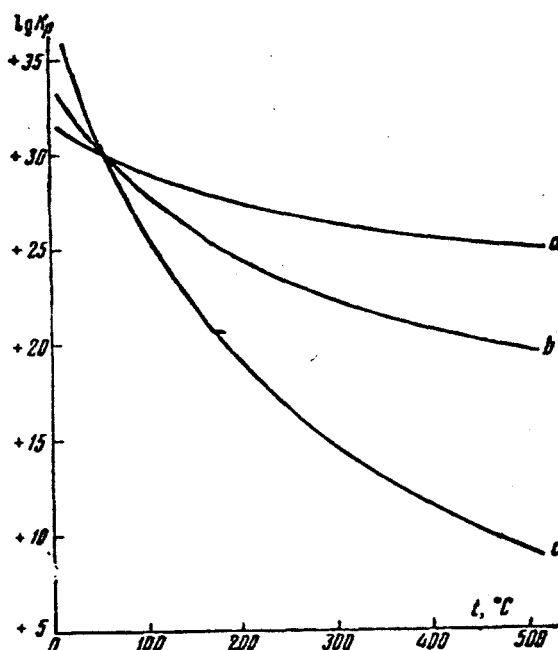

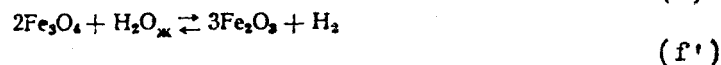Fig. 2. Curves $\lg K_p = f(T)$ of the oxidation reactions of siderite and magnetite oy free oxygen.
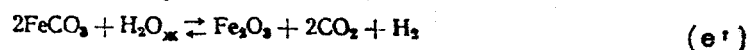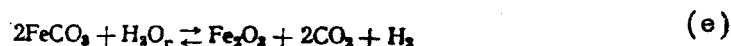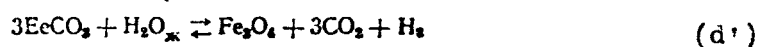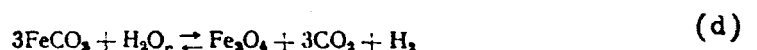
is very small amounting to only 10^{-50} atmospheres. When P_{O_2} is raised, reaction (a) should develop toward the formation of magnetite, and when it is lowered toward the formation of siderite. The oxidation of magnetite to hematite

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in reaction (c) at the same temperature calls for the maintenance of over $10^{-18.2}$ atmospheres throughout the P_{O_2} reaction. The above-discussed reactions at temperatures below $500°$ are characterized by still smaller magnitudes of equilibrium P_{O_2}.

An increase in the general pressure expressed by the total amount of partial gas pressure in the reaction should shift the equilibrium in the reactions (a) and (b) toward the formation of siderite. This increases the equilibrium P_{O_2} somewhat, but even at a pressure of 10,000 atmospheres and a temperature of $500°$, it still amounts to only 10^{-26} atmospheres for a siderite-magnetite association.

Thus in the metamorphism of the ferruginous-siliceous formations, siderite and magnetite could remain stable only under very low partial oxygen pressures. This conclusion does not contradict G. P. Eigster's data (1961), but the values lg K_p and, therefore also, a value of the equilibrium P_{O_2} we have obtained, are somewhat different from the previously published ones, which is due to the difference in the calculation methods and possibly also the difference in the initial thermodynamic values.

Of considerably greater interest are the results of the thermodynamic study of the assumed oxidation reactions of siderite and magnetite by water in the absence of free oxygen:

$$3FeCO_3 + H_2O_r \rightleftarrows Fe_3O_4 + 3CO_2 + H_2 \qquad \text{(d)}$$
$$3FeCO_3 + H_2O_{\text{ж}} \rightleftarrows Fe_3O_4 + 3CO_2 + H_2 \qquad \text{(d')}$$

$$2FeCO_3 + H_2O_r \rightleftarrows Fe_2O_3 + 2CO_2 + H_2 \qquad \text{(e)}$$
$$2FeCO_3 + H_2O_{\text{ж}} \rightleftarrows Fe_2O_3 + 2CO_2 + H_2 \qquad \text{(e')}$$

$$2Fe_3O_4 + H_2O_r \rightleftarrows 3Fe_2O_3 + H_2 \qquad \text{(f)}$$
$$2Fe_3O_4 + H_2O_{\text{ж}} \rightleftarrows 3Fe_2O_3 + H_2 \qquad \text{(f')}$$

Calculations show that siderite is stable at relatively low temperatures in the presence of gaseous or liquid water. At $25°$ the equilibrium constants of the oxidation reaction of siderite are considerably less than 1 (3), but as

the temperature rises the equilibrium shifts toward the formation of magnetite through the oxidation of siderite by water in a medium that does not contain any free oxygen or is characterized by an extremely low P_{O_2} value. Above 140°, the equilibrium constants of the oxidation reaction of siderite by water to magnetite are higher than 1, and at 400° they amount to $10^{9.1}$ in reaction (f) and $10^{11.6}$ in reaction (d'). The equilibrium constants of the oxidation reaction of magnetite to hematite by water in the temperature range under study is considerably lower than 1 (from $10^{-7.4}$ to 10^{-2}).

A comparison of the $\lg K_p = f(T)$ curves of reactions (d) and (e) with reaction (f) justifies the conclusion that siderite is unstable in the presence of water at temperatures above $140-150^o$ under low pressures and in its conversion to magnetite. There should be no further oxidation of magnetite to hematite in reaction (f) in the presence of siderite. The formation or balanced existence of a paragenetic siderite-magnetite-hematite association during the metamorphism is not very probable, inasmuch as the siderite-magnetite and magnetite-hematite associations, in the words of G. P. Eigster (1961), should be considered as individual buffered associations, each of them characterized by a strictly defined equiponderant partial pressure of water vapor, at a given temperature and pressure, which does not depend on the relative solid phase masses. A deflection of the P_{H_2O} from the equiponderant siderite-magnetite association will change the relative quantities of siderite and magnetite until P_{H_2O} returns to the initial equilibrium value. At the same time, the oxidation of magnetite to hematite will be impossible until the siderite is fully oxidized and P_{H_2O} exceeds the equilibrium value of the next buffered association of magnetite-hematite.

Characteristically, in all the discussed reactions carried out at temperatures above 100°, the equilibrium constant of the oxidation reactions of siderite and magnetite by liquid water -- (d'), (e') and (f') -- exceed the equilibrium

constants of similar reactions that include gaseous water -- (d), (e) and (f);

however, the lg $K_p = f(T)$ curves of the first and second groups of reactions

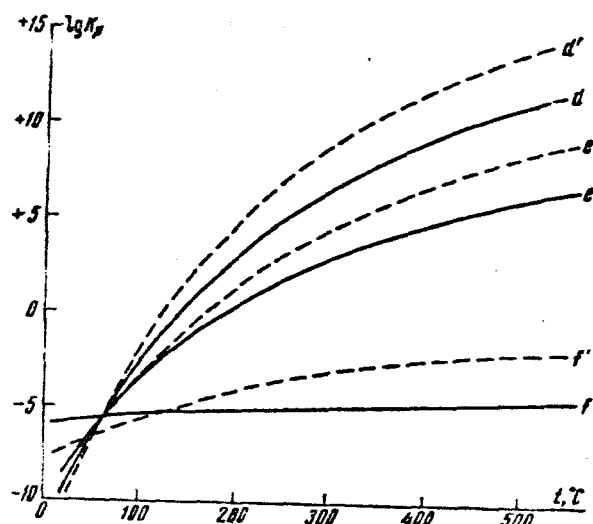are similar in nature, the only difference between them being the lg K_p magnitude.

Fig. 3. Curves lg $K_p = f(T)$ of the oxidation reactions of
siderite and magnetite by liquid and gaseous water.

Hence the very important conclusion that the state of aggregation of the water

in the reactions under consideration does not materially affect the direction of

the irreversible reactions at high temperatures, and produces only a minor change

in the equilibrium constants and, consequently, in the stability range of the

minerals. It would therefore by justifiable, in the cases under consideration,

to extend the general conclusions produced by a thermodynamic analysis of the

processes involving only gaseous water through the processes occurring under

supercritical pressures where the state of aggregation of the solutions (fluids)

is still not too well known.

Raising the equilibrium pressure in reactions (d) and (e) should, according

to the LeChatelier principle, change the reaction process toward the formation

of siderite. Inasmuch as a direct oxidation of siderite to hematite by water is

hardly probable, we will review in detail only the basic oxidation reaction of

siderite to magnetite at high temperatures and pressures. The equilibrium partial

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pressures for the siderite-magnetite association were determined from the nomogram (Fig. 1). The general pressure in this case was considered as the sum of the partial pressures of the gaseous components within the system

$$P_{gen.} = P_{H_2O} + P_{CO_2} + P_{H_2}.$$

The results obtained can be graphically expressed on diagrams as coordinates $lg\ P_{H_2O}$, $lg\ P_{CO_2}$, $lg\ P_{H_2}$. Inasmuch as the equilibrium constant of the reaction and, therefore also, the magnitude of equilibrium partial pressures of the gas phases are also a function of the temperature, it is possible to show on these diagrams the ratios of equiponderant partial pressures of the components under constant pressure ($P_{gen} =$ const) and various temperature, or at a constant temperature ($T =$ const) and variable pressure. The diagram presented in Figure 4 is for the study of the buffered association of siderite-magnetite at a constant
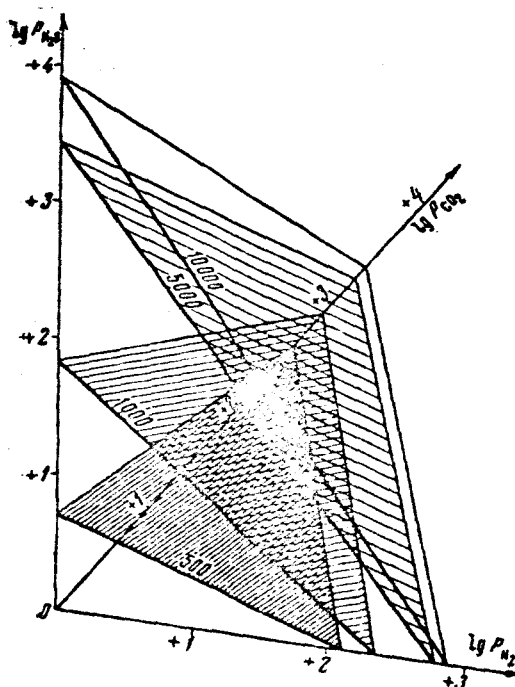

Fig. 4. Diagram of partial pressures H_2O, CO_2 and H_2 in a state of equilibrium with the siderite-magnetite association at a temperature of $400°$ and under a total pressure of 500, 1,000, 5,000, and 10,000 atmospheres.

temperature of $400°$ and pressures of 500, 1,000, 5,000 and 10,000 atmospheres. The equiponderant partial pressures of the components (or the composition of the

equilibrium gas mixture) at intermediate points of the total pressure can be determined by the analytical method which is to supplement the nomogram with a curve $\lg K_p = f(x)$ when the pressure is unknown, or by the graphical interpolation method and the use of the diagram (figure 4).

Comparing the equiponderant partial pressures of the components at 400° and varying the total pressure, determined from the diagram (Fig. 4), as for example, at 1,000 and 5,000 atmospheres, it is possible to prove the relationship between the composition of the equilibrium gas mixture and the pressure.

Under pressure of 1,000 atmospheres, the gas mixture equiponderant with the siderite-magnetite association is characterized by the following composition (in partial pressures) at a temperature of 400°: $P_{H_2O} = 65$ atmospheres, $P_{CO_2} = 700$ atmospheres; $P_{H_2} = 235$ atmospheres, ratio $P_{H_2O} / P_{gen.} = 0.065$.

Under pressure of 5,000 atmospheres the composition of the equilibrium gas mixtures for the same association at 400° is: $P_{H_2O} = 2,640$ atmospheres, $P_{CO_2} = 1,770$ atmospheres, $P_{H_2} = 590$ atmospheres, ratio $P_{H_2O} / P_{gen.} = 0.528$.

Thus, an increase in the total pressure results not only in the absolute but also in the relative increase of the equiponderant P_{H_2O}.

In the case of the reaction under consideration, an increase in the total pressure changes the equilibrium toward the formation of siderite. This relationship can be demonstrated graphically by a diagram (Fig. 5) in which the coordinates $\lg P_{gen.}$ and $\lg P_{H_2O}$ represent the stability range of siderite and magnetite at different temperatures. The curves delimiting the mentioned ranges show that magnetite and siderite maintain a stable resistance in a paragenetic association. The diagram clearly reveals the reverse effect of the temperature and pressure on the stability of siderite and magnetite. An increase in temperature widens the stability range of magnetite, and an increase in pressure reduces that stability range, and widens the stability range of siderite accordingly. The magnitude of the equilibrium partial water pressure for the siderite-magnetite

association, at any unknown temperature and pressure, can be found from the diagram.

A Discussion of the Results and the Geological Conclusions

The paragenetic siderite-magnetite association is widespread in the Ferruginous-siliceous rocks of the lower and middle stages of metaphorism in the Pre-Cambrian iron ore formations of Krivoy Rog, Kurst Magnetic Anomaly, Lake Superior 'U.S), Minas Geraes (Brazil), etc. Many researchers believe that in these rocks magnetite represents a metamorphic mineral developed from the primary sedimentary ore diagenetic siderite (Gershoig, 1932; Svital'skiy, 1932; Kanibolotskiy, 1946; Tochilin, 1952). Some authors, particularly P. P. Nazarov (1958), reject the possibility of siderite developing into magnetite, and believe that a reverse process took place during the metamorphism -- the development of siderite from magnetite. In a number of studies, mostly by American authors, the formation of iron ore minerals in various stages of oxidation, including siderite, magnetite and hematite, is explained by the Eh and pH fluctuations during the sedimentation period (Sakamote, 1950; James, 1954). The composition and interaction of these minerals was not materially changed in the metamorphism that followed. According to M. S. Tochilin (1963), the primary
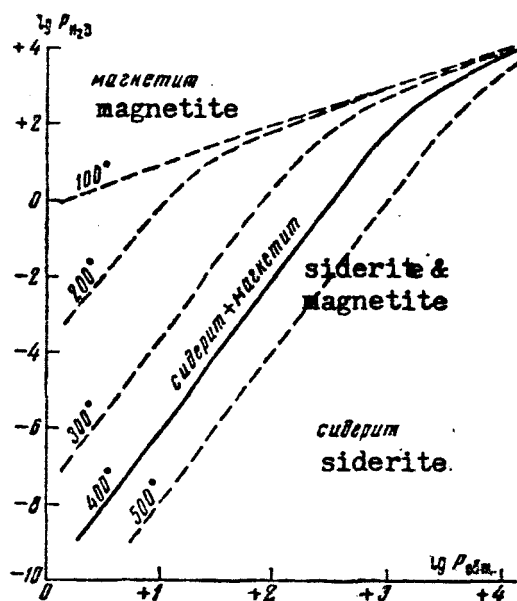

Fig. 5. Stability ranges of siderite and magnetite as determined
by lg P_{gen}, lg P_{H_2O} and temperature.

formation of magnetite and hematite in ferruginous quartzite was based on the inflow of iron from the fumarols and other sources during the underwater volcanism. The assertions made by Yu. Yu. Yurk and Ye. F. Shnyukov (1958; 1961) and a number of other authors to the effect that magnetite is a product of the progressive metamorphism of hydroxides are considered by M. S. Tochilin as erroneous.

Even this very incomplete review of the existing ideas of the origin of magnetite, and the relations between magentite and siderite, shows that many important problems related to the genesis of the ore materials of the ferruginous formations still remain unsolved.

A thermodynamic analysis facilitates a critical examination of certain debatable questions, particularly a determination of the stability range of siderite, magnetite and hematite at temperatures and pressures existing during the metamorphism.

The ferruginous quartzites and shales under consideration are classified by N. P. Semenenko (1954) as a group of metamorphic shales formed at temperatures up to 375-400°. According to F. Turner and J. Ferkhugen (1961), the temperature in the period of the formation of metamorphic rock of the green shale facies fluctuated from 300 to 500°. V. S. Sobolev (1961) estimates the temperature of the lower boundary of the regional metamorphism, on the basis of kaolin, at 450-500°, and the boundary of the low-temperature and medium-temperature metamorphism, on the basis of chlorite, at 600°. The pressure, according to various authors, could have fluctuated from 1,000 to 8,000 atmospheres.

In these conditions, siderite is obviously unstable in the presence of liquid or gaseous water, and should change to magnetite by releasing carbon dioxide and hydrogen. Above 400°, siderite can maintain a stable existence only under very high pressures (above 5,000 atmospheres), or at insignificant partial water pressure (Fig. 5). Inasmuch as siderite occurs in paragenetic association with magnetite or, less often, without it, in the ferruginous

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quartzite everywhere in the Krivoy Rog region, it should be assumed that either the metamorphism temperature of these rocks was below 400°, or that the amount of water in the interstitial solutions (fluids) was very limited. In the latter case, the buffered siderite-magnetite association could exist in equilibrium with a gas mixture characterized by a relatively low P_{H_2O} and high P_{CO_2} and P_{H_2}. The addition of water to the metamorphosed rock would have led (assuming a constant total pressure) to a higher P_{H_2O} and a change in the relative mass of siderite and magnetite. The quantity of water required to oxidize all the siderite in the ferruginous quartzite (even assuming that all the magnetite of these rocks had been formed by siderite), is not very large and fully comparable to the quantity of water released by the dehydration of the ferruginous-quartzite depositions.

Thus a quite satisfactory explanation is found for the assumption that at least some magnetite of the ferruginous-siliceous rock was produced by the hydration of the original sedimentary or diagenetic siderite during the metamorphism. The reverse process, that is the development of siderite from magnetite on a large scale could hardly have taken place in the progressive stage of metamorphism. Only at low temperatures, below 150-200°, and high P_{CO_2} can the reactions (d) and (d') result in the formation of siderite. Such phenomena, particularly the genesis of magnetite and even martite ores cemented by siderite were observed at Krivoy Rog, the Kursk Magnetic Anomaly and certain other areas, but their formation is associated primarily with the zone of hypergenesis.

The formation of magnetite from hematite and ferric hydrates could hardly have taken place during the metamorphism of ferruginous quartzites and shales, which agrees with M. S. Tochilin's concepts (1963). Reaction (c) may result in the formation of magnetite only at extremely low P_{O_2} magnitudes, or at temperatures considerably greater than the permissible magnitude for low-temperature metamorphism. What is meant here is the metamorphism of purely oxide sedimentations which do not contain any ferrous iron, or other reducing

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agents. Such low P_{O_2} magnitudes in these rocks are hardly possible in the presence of water. An increase in pressure also disturbs the equilibrium in favor of hematite formation, and should not facilitate its change to magnetite. Thus hematite should be considered as a stable mineral in low-and medium-temperature metamorphism. But under natural conditions, some of the hematite could have been reduced by the hydrogen released in the siderite hydration process; that is why the ferruginous quartzite and shales produced by the metamorphism of mixed siderite-magnetite-hematite rocks should consist primarily of magnetites.

It would also be interesting to make a critical examination of M. S. Tochilin's hypotheses (1963) of the possible oxidation of magnetite to martite by water in the process of metamorphism. This assumption is obviously erroneous, as may be seen from the position of the curves $\lg K_p = f(T)$ in figure 3 for reactions (f) and (f'). At 400°, the equilibrium constant of the oxidation of magnetite by water vapor which, in the opinion of M. S. Tochilin possesses considerably more energy than liquid water, amounts to only 2×10^{-4}. An increase in pressure should not facilite a straight course of this reaction but should change the equilibrium toward the formation of magnetite inasmuch as the water is in a liquid phase under supercritical pressures. The conversion of magnetite to martite by water in the absence of free oxygen during the meta-morphism requires the maintenance of a very high P_{H_2O} and extremely low P_{H_2} for the entire duration of the process. The fulfillment of this condition calls for the inflow of large quantities of "pure" (in G. Eigster's words) water into the metamorphosed rocks, and the simultaneous elimination of the hydrogen formation. The required quantities of water could not be produced by the dehydration of the ferruginous-siliceous depositions or the basement rock underneath them. Thus the hypothetic conversion of magnetite to martite by water in geological conditions could not produce a very important effect, although local manifestations of that process in special conditions, as for

example, in the formation of hydrothermal veins in ferruginous rocks, cannot be ruled out.

The above data justify the assumption that not only the changes in P_o, as indicated earlier by G. P. Eigster (1961), but also the changes in the partial pressure of water and other volatile substances affect the equilibrium of the reduction-oxidation reactions. Characteristic of such reactions, particularly reactions involving water, is the strong effect produced by the changing temperature on the equilibrium constant. The number of variable determining the mineral facies in such cases should therefore include not only the temperature and pressure but also the volatile components of the partial pressure, including water.

This can be illustrated by the example of the above discussed siderite-magnetite association. This association occurs in the Krivoy Rog region together with chlorites, cericite and other high-content minerals in the ferruginous quartzites and schists which may be classified, according to N. P. Semenenko's system (1954), as a group of metamorphic schists of the slate stage of the phyllite stage. Such rocks are characterized by the lowest temperature, and they determine the low temperature boundary of the dynamothermal metamorphism. The above-cited data on the stability of siderite justify the assumption that such rocks could have been formed in the presence of excessive water (a fairly high P_{H_2O}) and at a temperature up to 300°.

The same siderite-magnetite association in Krivoy Rog and certain magnetic anomalies of the Ukrainian shield occasionally occur paragenetically with amphiboles of the actinolite or cummingtonite type of transition rocks between low- and medium-temperature rocks. The stable existence of siderite in such rocks, formed at temperatures of $500-600^o$, is possible only at very low P_{H_2O}. Comparing the paragenetic associations of the siderite-containing rocks with the conditions of their formation, it is possible to conclude that in the cases under consideration the progressive metamorphism, especially its medium-and high-

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temperature stages, apparently occurred in conditions of limited quantities of water, as was pointed out earlier by V. A. Nikolayev (1947) and Kh. Yoder (1957).

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